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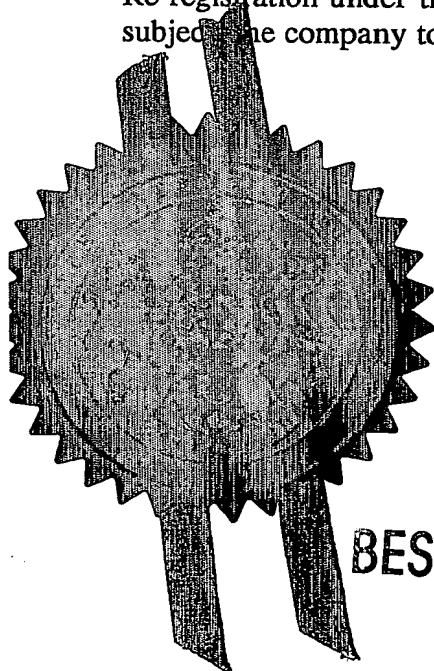
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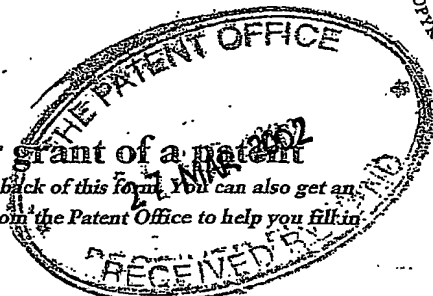
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1. Your reference PPD 50702/GB/P

2. Patent application number  
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0207253.6

27 MAR 2002

3. Full name, address and postcode of the or of each applicant (underline all surnames)  
SYNGENTA Participations AG  
Intellectual Property Department  
Schwarzwaldallee 215  
CH-4058 Basel  
SWITZERLAND

Patents ADP number (if you know it)

80 29555001

If the applicant is a corporate body, give the country/state of its incorporation

SWITZERLAND

4. Title of the invention CHEMICAL COMPOUNDS

5. Name of your agent (if you have one)

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UNITED KINGDOM

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Country

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7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

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8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

a) any applicant named in part 3 is not an inventor, or

b) there is an inventor who is not named as an applicant, or

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Description  
Claim(s) 03  
Abstract 01  
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Priority documents

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Statement of inventorship and right to grant of a patent (*Patents Form 7/77*)

Request for preliminary examination and search (*Patents Form 9/77*)

Request for substantive examination (*Patents Form 10/77*)

Any other documents  
(*please specify*)

11.

I/We request the grant of a patent on the basis of this application  
Syngenta Participations AG

Signature  
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Date

12. Name and daytime telephone number of person to contact in the United Kingdom

*Joanna Chandler*  
Joanna Carmen CHANDLER 01344 414365

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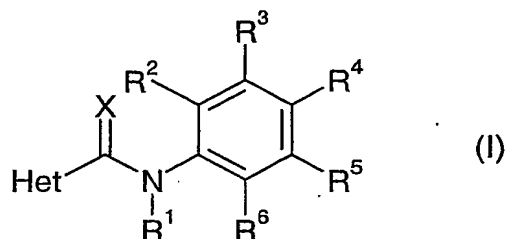
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CHEMICAL COMPOUNDS

The present invention relates to novel phenyl amides, substituted in the 2-position of the phenyl ring by a silicon containing substituent, which have microbiocidal activity, in particular fungicidal activity. The invention also relates to the preparation of these compounds, to novel intermediates used in the preparation of these compounds, to agrochemical compositions which comprise at least one of the novel compounds as active ingredient, to the preparation of the compositions mentioned and to the use of the active ingredients or compositions in agriculture or horticulture for controlling or preventing infestation of plants by phytopathogenic microorganisms, preferably fungi.

The present invention provides a compound of formula (I)



where Het is a 5- or 6-membered heterocyclic ring containing one to three heteroatoms, each independently selected from oxygen, nitrogen and sulphur, the ring being substituted by groups  $R^7$ ,  $R^8$  and  $R^9$ ;

$R^1$  is hydrogen, optionally substituted  $(C_{1-4})$ alkyl, optionally substituted  $(C_{1-4})$ alkylC(=O), optionally substituted  $(C_{1-4})$ alkylC(=O)O, optionally substituted  $(C_{1-4})$ alkoxy $(C_{1-4})$ alkyl, optionally substituted allyl, optionally substituted propargyl or optionally substituted allenyl;

$R^2$ ,  $R^3$ ,  $R^4$  and  $R^5$  are each, independently, hydrogen, halogen, optionally substituted  $(C_{1-4})$ alkyl, optionally substituted  $(C_{1-4})$ alkoxy or optionally substituted  $(C_{1-4})$ alkoxy $(C_{1-4})$ alkyl;

$R^6$  is an aliphatic or alicyclic, saturated or unsaturated group containing three to thirteen carbon atoms and at least one silicon atom and, optionally, one to three heteroatoms, each

independently selected from oxygen, nitrogen and sulphur, and is optionally substituted by one to four independently selected halogen atoms;

$R^7$ ,  $R^8$  and  $R^9$  are each, independently, hydrogen, halogen,  $C_{1-3}$  alkyl,  $C_{1-3}$  haloalkyl,  $C_{1-3}$ alkoxy( $C_{1-3}$ )alkyl or cyano, where at least one of  $R^7$ ,  $R^8$  and  $R^9$  is not hydrogen; and

5       X is O or S;  
or an N-oxide thereof.

Halogen is fluorine, chlorine, bromine or iodine, preferably fluorine, chlorine or bromine.

Each alkyl moiety is a straight or branched chain and is, for example, methyl, ethyl,  
10    *n*-propyl, *n*-butyl, *iso*-propyl, *n*-butyl, *sec*-butyl, *iso*-butyl or *tert*-butyl.

The alkenyl moieties, where appropriate, can be of either the (*E*)- or (*Z*)-configuration.

When present, each optional substituent on alkyl moieties, allyl, propargyl and allenyl is, independently, selected from halogen, hydroxy, cyano, carboxyl, methoxycarbonyl, ethoxycarbonyl, methoxy, ethoxy, methylsulfonyl, ethylsulfonyl, difluoromethoxy,  
15   trifluoromethoxy and trifluorothiomethoxy.

Preferably  $R^1$  is hydrogen, propargyl, allenyl,  $CH_3C(=O)$ ,  $C_2H_5C(=O)$  or  $CH_3OCH_2C(=O)$ .

Most preferably  $R^1$  is hydrogen.

Preferably  $R^2$ ,  $R^3$ ,  $R^4$  and  $R^5$  are each, independently, selected from hydrogen, halogen,  
20   methyl, trifluoromethyl and trifluoromethoxy.

More preferably  $R^2$ ,  $R^3$ ,  $R^4$  and  $R^5$  are each hydrogen.

It is preferred that Het is pyrazolyl, pyrrolyl, thiophenyl, furyl, thiazolyl, isothiazolyl, oxazolyl, isoxazolyl, triazolyl, pyridinyl, pyrazinyl, pyrimidinyl, pyridazinyl,  
5.6-dihydropyran or 5.6-dihydro-1.4-oxathiinyl (more preferably pyrazolyl, pyrrolyl,  
25   thiophenyl, furyl, thiazolyl, oxazolyl, pyridinyl, pyrimidinyl, pyridazinyl, 5.6-dihydropyran or 5.6-dihydro-1.4-oxathiinyl) each being substituted by groups  $R^7$ ,  $R^8$  and  $R^9$ .

Preferably  $R^6$  is  $Y^1-Si(O_mMe)(O_nMe)(O_pY^2)$  where  $m$ ,  $n$  and  $p$  are each, independently, 0 or 1;  $Y^1$  is a bond or is branched or unbranched alkandiyl, alkendiyl, or alkendiyl, containing 1-6 carbon atoms, optionally interrupted by one or two oxygen atoms and optionally  
30   substituted by up to three independently selected halogen atoms; and  $Y^2$  is alkyl or alkenyl, branched or unbranched, containing 1-5 carbon atoms and optionally interrupted by one

heteroatom selected from O, S and N and optionally substituted by up to three independently selected halogen atoms; and two non-adjacent carbons of  $Y^1$  or two non-adjacent carbons of  $Y^2$  or one carbon of  $Y^1$  and one carbon of  $Y^2$  may together form a bond to complete a cycle of ring size 3-7.

- 5 More preferably  $R^6$  is  $SiMe_3$ ,  $SiMe_2Et$ ,  $SiMe_2CHMe_2$ ,  $SiMe_2CH_2CHMe_2$ ,  $SiMe_2CH_2CMe_3$ ,  $SiMe_2OCHMe_2$ ,  $SiMe_2OCH_2CHMe_2$ ,  $CH_2SiMe_3$ ,  $CH_2SiMe_2Et$ ,  $CH_2SiMe_2CHMe_2$ ,  $CH_2SiMe_2CH_2CHMe_2$ ,  $CH_2SiMe_2OMe$ ,  $CH_2SiMe_2OCHMe_2$ ,  $CH_2SiMe_2OCH_2CHMe_2$ ,  $CHMeSiMe_3$ ,  $CHMeSiMe_2OMe$ ,  $(CH_2)_2SiMe_3$ ,  $(CH_2)_2SiMe_2Et$ ,  $(CH_2)_2SiMe_2CHMe_2$ ,  $(CH_2)_2SiMe_2CMe_3$ ,  $(CH_2)_2SiMe_2CH_2CHMe_2$ ,  $(CH_2)_2SiMe_2CH_2CMe_3$ ,  $(CH_2)_2SiMe_2OCHMe_2$ ,  $(CH_2)_2SiMe_2OCH_2CHMe_2$ ,  $CHMeCH_2SiMe_3$ ,  $CHMeCH_2SiMe_2Et$ ,  $CHMeCH_2SiMe_2CHMe_2$ ,  $CHMeCH_2SiMe_2CMe_3$ ,  $CHMeCH_2SiMe_2CH_2CHMe_2$ ,  $CFMeCH_2SiMe_3$ ,  $CHMeCH_2CH_2SiMe_2OMe$ ,  $CHMeCH_2SiMe_2OCHMe_2$ ,  $CHMeCH_2SiMe_2OCH_2CHMe_2$ ,  $(CH_2)_3SiMe_3$ ,  $(CH_2)_3SiMe_2Et$ ,  $(CH_2)_3SiMe_2CHMe_2$ ,  $(CH_2)_3SiMe_2CH_2CHMe_2$ ,  $(CH_2)_3SiMe_2OMe$ ,  $(CH_2)_3SiMe_2OCHMe_2$ ,  $(CH_2)_3SiMe_2OCH_2CHMe_2$ ,  $CHMeCH_2CH_2SiMe_3$ ,  $CHMeCH_2CH_2SiMe_2Et$ ,  $CHMeCH_2CH_2SiMe_2CHMe_2$ ,  $CHMeCH_2CH_2CH_2SiMe_2OMe$ ,  $CHMeCH_2CH_2SiMe_2OCHMe_2$ ,  $CMe=CHSiMe_3$ ,  $cyclo(C_3H_5)SiMe_3$  or  $CH_2CH_2SiMe_2OMe$ .
- 10  $CHMeCH_2CH_2SiMe_2CHMe_2$ ,  $CHMeCH_2CH_2CH_2SiMe_2OMe$ ,  $CHMeCH_2CH_2SiMe_2OCHMe_2$ ,  $CHMeCH_2CH_2CH_2SiMe_2CHMe_2$ ,  $CHMeCH_2CH_2CH_2CH_2SiMe_2OMe$ ,  $CHMeCH_2CH_2SiMe_2OCHMe_2$ ,  $CMe=CHSiMe_3$ ,  $cyclo(C_3H_5)SiMe_3$  or  $CH_2CH_2SiMe_2OMe$ .
- 15  $CHMeCH_2CH_2SiMe_2CHMe_2$ ,  $CHMeCH_2CH_2CH_2SiMe_2OMe$ ,  $CHMeCH_2CH_2SiMe_2OCHMe_2$ ,  $CHMeCH_2CH_2CH_2SiMe_2CHMe_2$ ,  $CHMeCH_2CH_2CH_2CH_2SiMe_2OMe$ ,  $CHMeCH_2CH_2SiMe_2OCHMe_2$ ,  $CMe=CHSiMe_3$ ,  $cyclo(C_3H_5)SiMe_3$  or  $CH_2CH_2SiMe_2OMe$ .

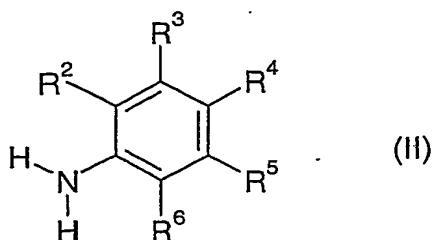
Preferably  $R^7$ ,  $R^8$  and  $R^9$  are each, independently, hydrogen, halogen, methyl,  $CF_3$ ,  $CF_2H$ ,  $CH_2F$ ,  $CF_2Cl$  or  $CH_2OCH_3$  (where at least one of  $R^7$ ,  $R^8$  and  $R^9$  is not hydrogen)

- 20 Preferably X is oxygen.

When the compounds of formula (I) are N-oxides then it is preferred that Het is pyridinyl, substituted by groups  $R^7$ ,  $R^8$  and  $R^9$ .

Throughout this description, Me is used to represent the methyl group. Likewise, Et represents the ethyl group.

- 25 Anilines of formula (II):



where  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  are as defined above for a compound of formula (I), are useful as intermediates in the preparation of compounds of formula (I).

5 Certain anilines of formula (II) are novel compounds. Therefore, in another aspect the present invention provides a compound of formula (II) where

$R^2$ ,  $R^3$ ,  $R^4$  and  $R^5$  are each, independently, hydrogen, halogen,  $CH_3$ ,  $CF_3$  or  $OCF_3$ ;  
 $R^6$  is  $(CHR^{10})(CR^{11}R^{12})_rSi(R^{13})(R^{14})(R^{15})$ ;  
 $r$  is 0, 1, 2 or 3;

10  $R^{10}$  is  $C_{1-3}$  alkyl or  $C_{1-3}$  haloalkyl; but if  $r$  is 2 or 3 then  $R^{10}$  may be also hydrogen;  
each  $R^{11}$  and each  $R^{12}$  is, independently, chosen from hydrogen, halogen,  $C_{1-3}$  alkyl and  $C_{1-3}$  haloalkyl;

$R^{13}$ ,  $R^{14}$  are, independently, methyl or ethyl; and  $R^{15}$  is  $C_{1-6}$  alkyl,  $C_{1-4}$  alkoxy( $C_{1-4}$ )alkyl,  $C_{1-3}$  haloalkyl,  $C_{2-6}$  alkenyl or  $C_{1-6}$  alkoxy;

15 or  $R^{10}$  and  $R^{11}$  on adjacent carbon atoms or two  $R^{11}$  groups on adjacent carbon atoms may together be a double bond or with the carbon atoms to which they are attached may form cyclopropyl which is optionally substituted by up to two substituents, independently chosen from halogen and methyl;  
or any two  $R^{11}$  groups or  $R^{10}$  and any one  $R^{11}$  may, together with the carbon atoms through  
20 which they are linked, form a cycloalkyl ring of ring size 4-7 which optionally contains 1 heteroatom selected from oxygen and sulfur and which is optionally substituted by up to two substituents, independently chosen from halogen and methyl; provided that  $R^6$  is such that the total number of C atoms is 5-13, the total number of halogen atoms is 0-4 and the number of heteroatoms is 0-3.

25 For a compound of formula (II), preferably  $R^2$ ,  $R^3$ ,  $R^4$  and  $R^5$  are each hydrogen.

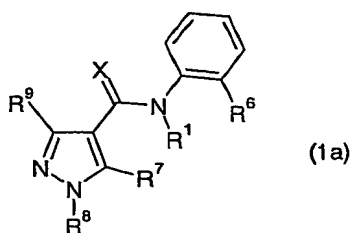
For a compound of formula (II), preferably  $R^6$  is  $CHMeSiMe_3$ ,  $CHMeSiMe_2OMe$ ,  
 $(CH_2)_2SiMe_2OCH_2CHMe_2$ ,  $CHMeCH_2SiMe_3$ ,  $CHMeCH_2SiMe_2Et$ ,  $CHMeCH_2SiMe_2CHMe_2$ ,  
 $CHMeCH_2SiMe_2CMe_3$ ,  $CHMeCH_2SiMe_2CH_2CHMe_2$ ,  $CFMeCH_2SiMe_3$ ,  
 $CHMeCH_2CH_2SiMe_2OMe$ ,  $CHMeCH_2SiMe_2OCHMe_2$ ,  $CHMeCH_2SiMe_2OCH_2CHMe_2$ ,  
30  $(CH_2)_3SiMe_3$ ,  $(CH_2)_3SiMe_2Et$ ,  $(CH_2)_3SiMe_2CHMe_2$ ,  $(CH_2)_3SiMe_2CH_2CHMe_2$ ,  
 $(CH_2)_3SiMe_2OMe$ ,  $(CH_2)_3SiMe_2OCHMe_2$ ,  $(CH_2)_3SiMe_2OCH_2CHMe_2$ ,  $CHMeCH_2CH_2SiMe_3$ ,

CHMeCH<sub>2</sub>CH<sub>2</sub>SiMe<sub>2</sub>Et, CHMeCH<sub>2</sub>CH<sub>2</sub>SiMe<sub>2</sub>CHMe<sub>2</sub>, CHMeCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SiMe<sub>2</sub>OMe, CHMeCH<sub>2</sub>CH<sub>2</sub>SiMe<sub>2</sub>OCHMe<sub>2</sub>, CMe=CHSiMe<sub>3</sub> or cyclo(C<sub>3</sub>H<sub>5</sub>)SiMe<sub>3</sub>.

The compounds of formula (I) and of formula (II) may exist as different geometric or optical isomers or in different tautomeric forms. This invention covers all such isomers and tautomers and mixtures thereof in all proportions as well as isotopic forms such as deuterated compounds.

The compounds in Tables 1 to 11 below illustrate compounds of the invention.

Table 1 provides 43 compounds of formula (Ia) where R<sup>1</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup> and X are as defined in Table 1.



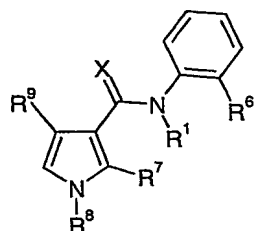
**Table 1**

| Compound No. | R <sup>1</sup> | R <sup>6</sup>                                    | R <sup>7</sup> | R <sup>8</sup> | R <sup>9</sup>    | X |
|--------------|----------------|---|----------------|----------------|-------------------|---|
| 1.1          | H              | SiMe <sub>3</sub>                                 | H              | Me             | CF <sub>3</sub>   | O |
| 1.2          | H              | SiMe <sub>3</sub>                                 | H              | Me             | CF <sub>2</sub> H | O |
| 1.3          | H              | CH <sub>2</sub> SiMe <sub>3</sub>                 | H              | Me             | CF <sub>3</sub>   | O |
| 1.4          | H              | CH <sub>2</sub> SiMe <sub>3</sub>                 | H              | Me             | CF <sub>3</sub>   | S |
| 1.5          | H              | CH <sub>2</sub> SiMe <sub>3</sub>                 | H              | Me             | CF <sub>2</sub> H | O |
| 1.6          | Propargyl      | CH <sub>2</sub> SiMe <sub>3</sub>                 | H              | Me             | CF <sub>3</sub>   | O |
| 1.7          | H              | CHMeSiMe <sub>3</sub>                             | H              | Me             | CF <sub>3</sub>   | O |
| 1.8          | H              | CHMeSiMe <sub>3</sub>                             | H              | Me             | CF <sub>2</sub> H | O |
| 1.9          | H              | CHMeSiMe <sub>3</sub>                             | H              | Me             | CF <sub>3</sub>   | S |
| 1.10         | Propargyl      | CHMeSiMe <sub>3</sub>                             | H              | Me             | CF <sub>3</sub>   | O |
| 1.11         | Allenyl        | CHMeSiMe <sub>3</sub>                             | H              | Me             | CF <sub>3</sub>   | O |
| 1.12         | COMe           | CHMeSiMe <sub>3</sub>                             | H              | Me             | CF <sub>3</sub>   | O |
| 1.13         | H              | CHMeSiMe <sub>3</sub>                             | F              | Me             | Me                | O |
| 1.14         | H              | (CH <sub>2</sub> ) <sub>2</sub> SiMe <sub>3</sub> | H              | Me             | CF <sub>3</sub>   | O |



|      |           |  |   |                         |                       |   |
|------|-----------|--|---|-------------------------|-----------------------|---|
| 1.15 | H         | $(\text{CH}_2)_2\text{SiMe}_3$                           | H | Me                      | $\text{CF}_3$         | S |
| 1.16 | H         | $(\text{CH}_2)_2\text{SiMe}_3$                           | H | Me                      | $\text{CF}_2\text{H}$ | O |
| 1.17 | Propargyl | $(\text{CH}_2)_2\text{SiMe}_3$                           | H | Me                      | $\text{CF}_3$         | O |
| 1.18 | H         | $(\text{CH}_2)_2\text{SiMe}_3$                           | F | Me                      | Me                    | O |
| 1.19 | H         | $(\text{CH}_2)_2\text{SiMe}_3$                           | H | $\text{CH}_2\text{OMe}$ | $\text{CF}_3$         | O |
| 1.20 | H         | $\text{CHMeCH}_2\text{SiMe}_3$                           | H | Me                      | $\text{CF}_3$         | O |
| 1.21 | H         | $\text{CHMeCH}_2\text{SiMe}_3$                           | H | Me                      | $\text{CF}_3$         | S |
| 1.22 | H         | $\text{CHMeCH}_2\text{SiMe}_3$                           | H | $\text{CH}_2\text{OMe}$ | $\text{CF}_3$         | O |
| 1.23 | H         | $\text{CHMeCH}_2\text{SiMe}_3$                           | H | Me                      | $\text{CF}_2\text{H}$ | O |
| 1.24 | H         | $\text{CHMeCH}_2\text{SiMe}_3$                           | H | Me                      | $\text{CF}_2\text{H}$ | S |
| 1.25 | Propargyl | $\text{CHMeCH}_2\text{SiMe}_3$                           | H | Me                      | $\text{CF}_3$         | O |
| 1.26 | Allenyl   | $\text{CHMeCH}_2\text{SiMe}_3$                           | H | Me                      | $\text{CF}_3$         | O |
| 1.27 | Propargyl | $\text{CHMeCH}_2\text{SiMe}_3$                           | H | Me                      | $\text{CF}_2\text{H}$ | O |
| 1.28 | Allenyl   | $\text{CHMeCH}_2\text{SiMe}_3$                           | H | Me                      | $\text{CF}_2\text{H}$ | O |
| 1.29 | H         | $\text{CHMeCH}_2\text{SiMe}_3$                           | F | Me                      | Me                    | O |
| 1.30 | COMe      | $\text{CHMeCH}_2\text{SiMe}_3$                           | H | Me                      | $\text{CF}_3$         | O |
| 1.31 | H         | $(\text{CH}_2)_3\text{SiMe}_3$                           | H | Me                      | $\text{CF}_3$         | O |
| 1.32 | H         | $(\text{CH}_2)_3\text{SiMe}_3$                           | H | Me                      | $\text{CF}_2\text{H}$ | O |
| 1.33 | H         | $\text{CH}_2\text{Si}(\text{Me}_2)\text{Et}$             | H | Me                      | $\text{CF}_3$         | O |
| 1.34 | H         | $\text{CH}_2\text{Si}(\text{Me}_2)\text{Et}$             | H | Me                      | $\text{CF}_2\text{H}$ | O |
| 1.35 | H         | $\text{CH}_2\text{Si}(\text{Me}_2)\text{CHMe}_2$         | H | Me                      | $\text{CF}_3$         | O |
| 1.36 | H         | $\text{CH}_2\text{Si}(\text{Me}_2)\text{CHMe}_2$         | H | Me                      | $\text{CF}_2\text{H}$ | O |
| 1.37 | H         | $\text{CH}_2\text{Si}(\text{Me}_2)\text{OMe}$            | H | Me                      | $\text{CF}_3$         | O |
| 1.38 | H         | $\text{CH}_2\text{Si}(\text{Me}_2)\text{OMe}$            | H | Me                      | $\text{CF}_2\text{H}$ | O |
| 1.39 | H         | $\text{CH}_2\text{CH}_2\text{Si}(\text{Me}_2)\text{OMe}$ | H | Me                      | $\text{CF}_3$         | O |
| 1.40 | H         | $\text{CHMeSi}(\text{Me}_2)\text{OMe}$                   | H | Me                      | $\text{CF}_3$         | O |
| 1.41 | H         | $\text{CHMeSi}(\text{Me}_2)\text{OMe}$                   | H | Me                      | $\text{CF}_2\text{H}$ | O |
| 1.42 | H         | $\text{CH}_2\text{CH}_2\text{Si}(\text{Me}_2)\text{OMe}$ | H | Me                      | $\text{CF}_2\text{H}$ | O |
| 1.43 | H         | $\text{C}(\text{Me})=\text{CHSiMe}_3$                    | H | Me                      | $\text{CF}_3$         | O |

Table 2 provides 42 compounds of formula (Ib) where  $R^1$ ,  $R^6$ ,  $R^7$ ,  $R^8$ ,  $R^9$  and X are as defined in Table 2.



(Ib)

**Table 2**

| Compound No. | $R^1$     | $R^6$   | $R^7$ | $R^8$               | $R^9$             | X |
|--------------|-----------|---|-------|---------------------|-------------------|---|
| 2.1          | H         | SiMe <sub>3</sub>                                 | H     | Me                  | CF <sub>3</sub>   | O |
| 2.2          | H         | SiMe <sub>3</sub>                                 | H     | Me                  | CF <sub>2</sub> H | O |
| 2.3          | H         | CH <sub>2</sub> SiMe <sub>3</sub>                 | H     | Me                  | CF <sub>3</sub>   | O |
| 2.4          | H         | CH <sub>2</sub> SiMe <sub>3</sub>                 | H     | Me                  | CF <sub>3</sub>   | S |
| 2.5          | H         | CH <sub>2</sub> SiMe <sub>3</sub>                 | H     | Me                  | CF <sub>2</sub> H | O |
| 2.6          | Propargyl | CH <sub>2</sub> SiMe <sub>3</sub>                 | H     | Me                  | CF <sub>3</sub>   | O |
| 2.7          | H         | CHMeSiMe <sub>3</sub>                             | H     | Me                  | CF <sub>3</sub>   | O |
| 2.8          | H         | CHMeSiMe <sub>3</sub>                             | H     | Me                  | CF <sub>2</sub> H | O |
| 2.9          | H         | CHMeSiMe <sub>3</sub>                             | H     | Me                  | CF <sub>3</sub>   | S |
| 2.10         | Propargyl | CHMeSiMe <sub>3</sub>                             | H     | Me                  | CF <sub>3</sub>   | O |
| 2.11         | Allenyl   | CHMeSiMe <sub>3</sub>                             | H     | Me                  | CF <sub>3</sub>   | O |
| 2.12         | COMe      | CHMeSiMe <sub>3</sub>                             | H     | Me                  | CF <sub>3</sub>   | O |
| 2.13         | H         | CHMeSiMe <sub>3</sub>                             | F     | Me                  | Me                | O |
| 2.14         | H         | (CH <sub>2</sub> ) <sub>2</sub> SiMe <sub>3</sub> | H     | Me                  | CF <sub>3</sub>   | O |
| 2.15         | H         | (CH <sub>2</sub> ) <sub>2</sub> SiMe <sub>3</sub> | H     | Me                  | CF <sub>3</sub>   | S |
| 2.16         | H         | (CH <sub>2</sub> ) <sub>2</sub> SiMe <sub>3</sub> | H     | Me                  | CF <sub>2</sub> H | O |
| 2.17         | Propargyl | (CH <sub>2</sub> ) <sub>2</sub> SiMe <sub>3</sub> | H     | Me                  | CF <sub>3</sub>   | O |
| 2.18         | H         | (CH <sub>2</sub> ) <sub>2</sub> SiMe <sub>3</sub> | F     | Me                  | Me                | O |
| 2.19         | H         | (CH <sub>2</sub> ) <sub>2</sub> SiMe <sub>3</sub> | H     | CH <sub>2</sub> OMe | CF <sub>3</sub>   | O |

|      |           |   |   |                     |                   |   |
|------|-----------|---|---|---------------------|-------------------|---|
| 2.20 | H         | CHMeCH <sub>2</sub> SiMe <sub>3</sub>                   | H | Me                  | CF <sub>3</sub>   | O |
| 2.21 | H         | CHMeCH <sub>2</sub> SiMe <sub>3</sub>                   | H | Me                  | CF <sub>3</sub>   | S |
| 2.22 | H         | CHMeCH <sub>2</sub> SiMe <sub>3</sub>                   | H | CH <sub>2</sub> OMe | CF <sub>3</sub>   | O |
| 2.23 | H         | CHMeCH <sub>2</sub> SiMe <sub>3</sub>                   | H | Me                  | CF <sub>2</sub> H | O |
| 2.24 | H         | CHMeCH <sub>2</sub> SiMe <sub>3</sub>                   | H | Me                  | CF <sub>2</sub> H | S |
| 2.25 | Propargyl | CHMeCH <sub>2</sub> SiMe <sub>3</sub>                   | H | Me                  | CF <sub>3</sub>   | O |
| 2.26 | Allenyl   | CHMeCH <sub>2</sub> SiMe <sub>3</sub>                   | H | Me                  | CF <sub>3</sub>   | O |
| 2.27 | Propargyl | CHMeCH <sub>2</sub> SiMe <sub>3</sub>                   | H | Me                  | CF <sub>2</sub> H | O |
| 2.28 | Allenyl   | CHMeCH <sub>2</sub> SiMe <sub>3</sub>                   | H | Me                  | CF <sub>2</sub> H | O |
| 2.29 | H         | CHMeCH <sub>2</sub> SiMe <sub>3</sub>                   | F | Me                  | Me                | O |
| 2.30 | COMe      | CHMeCH <sub>2</sub> SiMe <sub>3</sub>                   | H | Me                  | CF <sub>3</sub>   | O |
| 2.31 | H         | (CH <sub>2</sub> ) <sub>3</sub> SiMe <sub>3</sub>       | H | Me                  | CF <sub>3</sub>   | O |
| 2.32 | H         | (CH <sub>2</sub> ) <sub>3</sub> SiMe <sub>3</sub>       | H | Me                  | CF <sub>2</sub> H | O |
| 2.33 | H         | CH <sub>2</sub> Si(Me <sub>2</sub> )Et                  | H | Me                  | CF <sub>3</sub>   | O |
| 2.34 | H         | CH <sub>2</sub> Si(Me <sub>2</sub> )Et                  | H | Me                  | CF <sub>2</sub> H | O |
| 2.35 | H         | CH <sub>2</sub> Si(Me <sub>2</sub> )CHMe <sub>2</sub>   | H | Me                  | CF <sub>3</sub>   | O |
| 2.36 | H         | CH <sub>2</sub> Si(Me <sub>2</sub> )CHMe <sub>2</sub>   | H | Me                  | CF <sub>2</sub> H | O |
| 2.37 | H         | CH <sub>2</sub> Si(Me <sub>2</sub> )OMe                 | H | Me                  | CF <sub>3</sub>   | O |
| 2.38 | H         | CH <sub>2</sub> Si(Me <sub>2</sub> )OMe                 | H | Me                  | CF <sub>2</sub> H | O |
| 2.39 | H         | CH <sub>2</sub> CH <sub>2</sub> Si(Me <sub>2</sub> )OMe | H | Me                  | CF <sub>3</sub>   | O |
| 2.40 | H         | CHMeSi(Me <sub>2</sub> )OMe                             | H | Me                  | CF <sub>3</sub>   | O |
| 2.41 | H         | CHMeSi(Me <sub>2</sub> )OMe                             | H | Me                  | CF <sub>2</sub> H | O |
| 2.42 | H         | CH <sub>2</sub> CH <sub>2</sub> Si(Me <sub>2</sub> )OMe | H | Me                  | CF <sub>2</sub> H | O |

Table A represents Table 3 (when A is 3) and represents Table 4 (when A is 4).

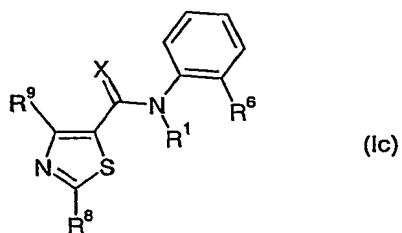
**Table A**

| Compound No. | R <sup>1</sup> | R <sup>6</sup>    | R <sup>8</sup> | R <sup>9</sup>    | X |
|--------------|----------------|-------------------|----------------|-------------------|---|
| A.1          | H              | SiMe <sub>3</sub> | Me             | CF <sub>3</sub>   | O |
| A.2          | H              | SiMe <sub>3</sub> | Me             | CF <sub>2</sub> H | O |

|      |           |   |                 |                   |   |
|------|-----------|---|-----------------|-------------------|---|
| A.3  | H         | CH <sub>2</sub> SiMe <sub>3</sub>                 | Me              | CF <sub>3</sub>   | O |
| A.4  | H         | CH <sub>2</sub> SiMe <sub>3</sub>                 | Me              | CF <sub>3</sub>   | S |
| A.5  | H         | CH <sub>2</sub> SiMe <sub>3</sub>                 | Me              | CF <sub>2</sub> H | O |
| A.6  | Propargyl | CH <sub>2</sub> SiMe <sub>3</sub>                 | Me              | CF <sub>3</sub>   | O |
| A.7  | H         | CHMeSiMe <sub>3</sub>                             | Me              | CF <sub>3</sub>   | O |
| A.8  | H         | CHMeSiMe <sub>3</sub>                             | Me              | CF <sub>2</sub> H | O |
| A.9  | H         | CHMeSiMe <sub>3</sub>                             | Me              | CF <sub>3</sub>   | S |
| A.10 | Propargyl | CHMeSiMe <sub>3</sub>                             | Me              | CF <sub>3</sub>   | O |
| A.11 | Allenyl   | CHMeSiMe <sub>3</sub>                             | Me              | CF <sub>3</sub>   | O |
| A.12 | COMe      | CHMeSiMe <sub>3</sub>                             | Me              | CF <sub>3</sub>   | O |
| A.13 | H         | CHMeSiMe <sub>3</sub>                             | Me              | Me                | O |
| A.14 | H         | (CH <sub>2</sub> ) <sub>2</sub> SiMe <sub>3</sub> | Me              | CF <sub>3</sub>   | O |
| A.15 | H         | (CH <sub>2</sub> ) <sub>2</sub> SiMe <sub>3</sub> | Me              | CF <sub>3</sub>   | S |
| A.16 | H         | (CH <sub>2</sub> ) <sub>2</sub> SiMe <sub>3</sub> | Me              | CF <sub>2</sub> H | O |
| A.17 | Propargyl | (CH <sub>2</sub> ) <sub>2</sub> SiMe <sub>3</sub> | Me              | CF <sub>3</sub>   | O |
| A.18 | H         | (CH <sub>2</sub> ) <sub>2</sub> SiMe <sub>3</sub> | Me              | Me                | O |
| A.19 | H         | (CH <sub>2</sub> ) <sub>2</sub> SiMe <sub>3</sub> | CF <sub>3</sub> | CF <sub>3</sub>   | O |
| A.20 | H         | CHMeCH <sub>2</sub> SiMe <sub>3</sub>             | Me              | CF <sub>3</sub>   | O |
| A.21 | H         | CHMeCH <sub>2</sub> SiMe <sub>3</sub>             | Me              | CF <sub>3</sub>   | S |
| A.22 | H         | CHMeCH <sub>2</sub> SiMe <sub>3</sub>             | Me              | CF <sub>2</sub> H | O |
| A.23 | H         | CHMeCH <sub>2</sub> SiMe <sub>3</sub>             | Me              | CF <sub>2</sub> H | S |
| A.24 | Propargyl | CHMeCH <sub>2</sub> SiMe <sub>3</sub>             | Me              | CF <sub>3</sub>   | O |
| A.25 | Propargyl | CHMeCH <sub>2</sub> SiMe <sub>3</sub>             | Me              | CF <sub>2</sub> H | O |
| A.26 | H         | CHMeCH <sub>2</sub> SiMe <sub>3</sub>             | Me              | Me                | O |
| A.27 | H         | CHMeCH <sub>2</sub> SiMe <sub>3</sub>             | CF <sub>3</sub> | CF <sub>3</sub>   | O |
| A.28 | COMe      | CHMeCH <sub>2</sub> SiMe <sub>3</sub>             | Me              | CF <sub>3</sub>   | O |
| A.29 | H         | (CH <sub>2</sub> ) <sub>3</sub> SiMe <sub>3</sub> | Me              | CF <sub>3</sub>   | O |
| A.30 | H         | (CH <sub>2</sub> ) <sub>3</sub> SiMe <sub>3</sub> | Me              | CF <sub>2</sub> H | O |
| A.31 | H         | CH <sub>2</sub> Si(Me <sub>2</sub> )Et            | Me              | CF <sub>3</sub>   | O |
| A.32 | H         | CH <sub>2</sub> Si(Me <sub>2</sub> )Et            | Me              | CF <sub>2</sub> H | O |

|      |   |   |    |                   |   |
|------|---|---|----|-------------------|---|
| A.33 | H | CH <sub>2</sub> Si(Me) <sub>2</sub> CHMe <sub>2</sub> | Me | CF <sub>3</sub>   | O |
| A.34 | H | CH <sub>2</sub> Si(Me) <sub>2</sub> CHMe <sub>2</sub> | Me | CF <sub>2</sub> H | O |

Table 3 provides 34 compounds of formula (Ic) where R<sup>1</sup>, R<sup>6</sup>, R<sup>8</sup>, R<sup>9</sup> and X are as defined in Table 3.



5 Table 4 provides 34 compounds of formula (Id) where R<sup>1</sup>, R<sup>6</sup>, R<sup>8</sup>, R<sup>9</sup> and X are as defined in Table 4.

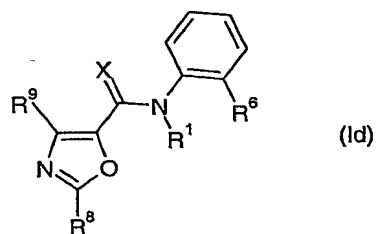


Table B represents Table 5 (when B is 5) and represents Table 6 (when B is 6).

**Table B**

| Compound No. | R <sup>1</sup> | R <sup>6</sup>                    | R <sup>7</sup> | R <sup>8</sup> | R <sup>9</sup>  | X |
|--------------|----------------|-----------------------------------|----------------|----------------|-----------------|---|
| B.1          | H              | SiMe <sub>3</sub>                 | Me             | Me             | H               | O |
| B.2          | H              | SiMe <sub>3</sub>                 | Me             | Me             | H               | O |
| B.3          | H              | CH <sub>2</sub> SiMe <sub>3</sub> | Me             | Me             | Me              | O |
| B.4          | H              | CH <sub>2</sub> SiMe <sub>3</sub> | Me             | Me             | CF <sub>3</sub> | O |
| B.5          | H              | CH <sub>2</sub> SiMe <sub>3</sub> | Me             | Me             | H               | O |
| B.6          | Propargyl      | CH <sub>2</sub> SiMe <sub>3</sub> | Me             | Me             | CF <sub>3</sub> | O |
| B.7          | H              | CHMeSiMe <sub>3</sub>             | Me             | Me             | CF <sub>3</sub> | O |

|      |           |   |    |    |                 |   |
|------|-----------|---|----|----|-----------------|---|
| B.8  | H         | CHMeSiMe <sub>3</sub>                             | Me | Me | Me              | O |
| B.9  | H         | CHMeSiMe <sub>3</sub>                             | Me | Me | Me              | S |
| B.10 | Propargyl | CHMeSiMe <sub>3</sub>                             | Me | Me | Me              | O |
| B.11 | Allenyl   | CHMeSiMe <sub>3</sub>                             | Me | Me | Me              | O |
| B.12 | COMe      | CHMeSiMe <sub>3</sub>                             | Me | Me | Me              | O |
| B.13 | H         | CHMeSiMe <sub>3</sub>                             | Me | Me | Me              | O |
| B.14 | H         | (CH <sub>2</sub> ) <sub>2</sub> SiMe <sub>3</sub> | Me | Me | CF <sub>3</sub> | O |
| B.15 | H         | (CH <sub>2</sub> ) <sub>2</sub> SiMe <sub>3</sub> | H  | H  | CF <sub>3</sub> | O |
| B.16 | H         | (CH <sub>2</sub> ) <sub>2</sub> SiMe <sub>3</sub> | H  | H  | CF <sub>3</sub> | S |
| B.17 | Propargyl | (CH <sub>2</sub> ) <sub>2</sub> SiMe <sub>3</sub> | H  | H  | CF <sub>3</sub> | O |
| B.18 | H         | (CH <sub>2</sub> ) <sub>2</sub> SiMe <sub>3</sub> | Me | Me | H               | O |
| B.19 | H         | CHMeCH <sub>2</sub> SiMe <sub>3</sub>             | H  | H  | CF <sub>3</sub> | O |
| B.20 | H         | CHMeCH <sub>2</sub> SiMe <sub>3</sub>             | H  | H  | CF <sub>3</sub> | S |
| B.21 | H         | CHMeCH <sub>2</sub> SiMe <sub>3</sub>             | Me | Me | Me              | O |
| B.22 | H         | CHMeCH <sub>2</sub> SiMe <sub>3</sub>             | H  | Me | CF <sub>3</sub> | O |
| B.23 | H         | CHMeCH <sub>2</sub> SiMe <sub>3</sub>             | Me | Me | H               | O |
| B.24 | COMe      | CHMeCH <sub>2</sub> SiMe <sub>3</sub>             | Me | Me | H               | O |
| B.25 | Propargyl | CHMeCH <sub>2</sub> SiMe <sub>3</sub>             | Me | Me | H               | O |
| B.26 | Allenyl   | CHMeCH <sub>2</sub> SiMe <sub>3</sub>             | Me | Me | H               | O |
| B.27 | Propargyl | CHMeCH <sub>2</sub> SiMe <sub>3</sub>             | Me | Me | Me              | O |
| B.28 | Allenyl   | CHMeCH <sub>2</sub> SiMe <sub>3</sub>             | Me | Me | Me              | O |
| B.29 | COMe      | CHMeCH <sub>2</sub> SiMe <sub>3</sub>             | Me | Me | Me              | O |
| B.30 | COEt      | CHMeCH <sub>2</sub> SiMe <sub>3</sub>             | Me | Me | Me              | O |

Table 5 provides 30 compounds of formula (Ie) where R<sup>1</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup> and X are as defined in Table 5.

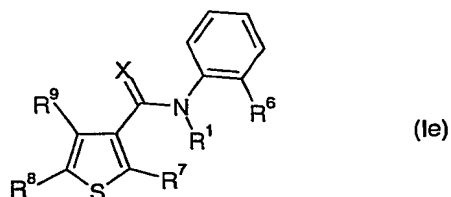
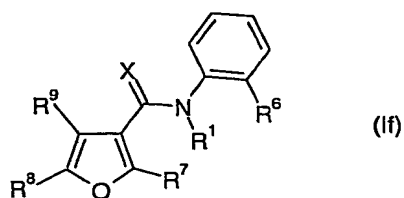


Table 6 provides 30 compounds of formula (If) where  $R^1$ ,  $R^6$ ,  $R^7$ ,  $R^8$ ,  $R^9$  and X are as defined in Table 6.



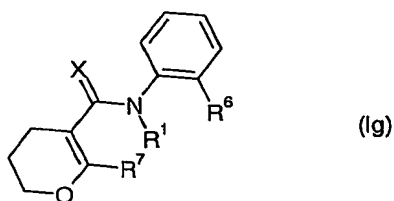
5 Table C represents Table 7 (when C is 7) and represents Table 8 (when C is 8).

**Table C**

| Compound No. | $R^1$     | $R^6$   | $R^7$           | X |
|--------------|-----------|---|-----------------|---|
| C.1          | H         | SiMe <sub>3</sub>                                 | Me              | O |
| C.2          | H         | SiMe <sub>3</sub>                                 | CF <sub>3</sub> | O |
| C.3          | H         | CH <sub>2</sub> SiMe <sub>3</sub>                 | Me              | O |
| C.4          | H         | CH <sub>2</sub> SiMe <sub>3</sub>                 | CF <sub>3</sub> | S |
| C.5          | COMe      | CH <sub>2</sub> SiMe <sub>3</sub>                 | Me              | O |
| C.6          | Propargyl | CH <sub>2</sub> SiMe <sub>3</sub>                 | Me              | O |
| C.7          | H         | CHMeSiMe <sub>3</sub>                             | Me              | O |
| C.8          | H         | CHMeSiMe <sub>3</sub>                             | CF <sub>3</sub> | O |
| C.9          | H         | CHMeSiMe <sub>3</sub>                             | CF <sub>3</sub> | S |
| C.10         | Propargyl | CHMeSiMe <sub>3</sub>                             | Me              | O |
| C.11         | Allenyl   | CHMeSiMe <sub>3</sub>                             | Me              | O |
| C.12         | COMe      | CHMeSiMe <sub>3</sub>                             | Me              | O |
| C.13         | Propargyl | CHMeSiMe <sub>3</sub>                             | CF <sub>3</sub> | O |
| C.14         | H         | (CH <sub>2</sub> ) <sub>2</sub> SiMe <sub>3</sub> | Me              | O |
| C.15         | H         | (CH <sub>2</sub> ) <sub>2</sub> SiMe <sub>3</sub> | CF <sub>3</sub> | O |

|      |           |                                |               |   |
|------|-----------|--------------------------------|---------------|---|
| C.16 | H         | $(\text{CH}_2)_2\text{SiMe}_3$ | $\text{CF}_3$ | S |
| C.17 | Propargyl | $(\text{CH}_2)_2\text{SiMe}_3$ | Me            | O |
| C.18 | COMe      | $(\text{CH}_2)_2\text{SiMe}_3$ | Me            | O |
| C.19 | H         | $\text{CHMeCH}_2\text{SiMe}_3$ | Me            | O |
| C.20 | H         | $\text{CHMeCH}_2\text{SiMe}_3$ | $\text{CF}_3$ | O |
| C.21 | H         | $\text{CHMeCH}_2\text{SiMe}_3$ | $\text{CF}_3$ | S |
| C.22 | Propargyl | $\text{CHMeCH}_2\text{SiMe}_3$ | Me            | O |
| C.23 | Allenyl   | $\text{CHMeCH}_2\text{SiMe}_3$ | Me            | O |
| C.24 | COMe      | $\text{CHMeCH}_2\text{SiMe}_3$ | Me            | O |
| C.25 | Propargyl | $\text{CHMeCH}_2\text{SiMe}_3$ | $\text{CF}_3$ | O |
| C.26 | Allenyl   | $\text{CHMeCH}_2\text{SiMe}_3$ | $\text{CF}_3$ | O |
| C.27 | COMe      | $\text{CHMeCH}_2\text{SiMe}_3$ | $\text{CF}_3$ | O |
| C.28 | Allenyl   | $\text{CHMeCH}_2\text{SiMe}_3$ | Me            | O |
| C.29 | H         | $(\text{CH}_2)_3\text{SiMe}_3$ | Me            | O |
| C.30 | H         | $(\text{CH}_2)_3\text{SiMe}_3$ | $\text{CF}_3$ | O |

Table 7 provides 30 compounds of formula (Ig) where  $\text{R}^1$ ,  $\text{R}^6$ ,  $\text{R}^7$  and X are as defined in Table 7.



5 Table 8 provides 30 compounds of formula (Ih) where  $\text{R}^1$ ,  $\text{R}^6$ ,  $\text{R}^7$  and X are as defined in Table 8.



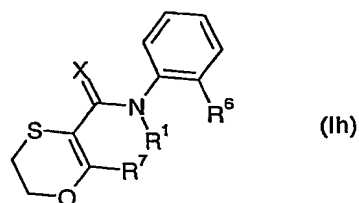


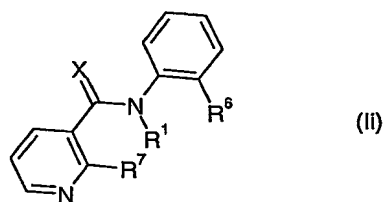
Table D represents Table 9 (when D is 9), represents Table 10 (when D is 10) and represents Table 11 (when D is 11).

**Table D**

| Compound No. | R <sup>1</sup> | R <sup>6</sup>                                    | R <sup>7</sup>  | X |
|--------------|----------------|---|-----------------|---|
| D.1          | H              | SiMe <sub>3</sub>                                 | Cl              | O |
| D.2          | H              | SiMe <sub>3</sub>                                 | CF <sub>3</sub> | O |
| D.3          | H              | CH <sub>2</sub> SiMe <sub>3</sub>                 | Cl              | O |
| D.4          | H              | CH <sub>2</sub> SiMe <sub>3</sub>                 | Br              | O |
| D.5          | H              | CH <sub>2</sub> SiMe <sub>3</sub>                 | CF <sub>3</sub> | O |
| D.6          | Propargyl      | CH <sub>2</sub> SiMe <sub>3</sub>                 | Cl              | O |
| D.7          | H              | CHMeSiMe <sub>3</sub>                             | Cl              | O |
| D.8          | H              | CHMeSiMe <sub>3</sub>                             | Br              | O |
| D.9          | H              | CHMeSiMe <sub>3</sub>                             | CF <sub>3</sub> | O |
| D.10         | Propargyl      | CHMeSiMe <sub>3</sub>                             | Cl              | O |
| D.11         | Allenyl        | CHMeSiMe <sub>3</sub>                             | Cl              | O |
| D.12         | COMe           | CHMeSiMe <sub>3</sub>                             | Cl              | O |
| D.13         | H              | CHMeSiMe <sub>3</sub>                             | Cl              | S |
| D.14         | H              | (CH <sub>2</sub> ) <sub>2</sub> SiMe <sub>3</sub> | Cl              | O |
| D.15         | H              | (CH <sub>2</sub> ) <sub>2</sub> SiMe <sub>3</sub> | Br              | O |
| D.16         | H              | (CH <sub>2</sub> ) <sub>2</sub> SiMe <sub>3</sub> | CF <sub>3</sub> | O |
| D.17         | Propargyl      | (CH <sub>2</sub> ) <sub>2</sub> SiMe <sub>3</sub> | Cl              | O |
| D.18         | COMe           | (CH <sub>2</sub> ) <sub>2</sub> SiMe <sub>3</sub> | Cl              | O |
| D.19         | H              | CHMeCH <sub>2</sub> SiMe <sub>3</sub>             | Cl              | O |
| D.20         | H              | CHMeCH <sub>2</sub> SiMe <sub>3</sub>             | Cl              | S |

|      |                       |   |                 |   |
|------|-----------------------|---|-----------------|---|
| D.21 | H                     | CHMeCH <sub>2</sub> SiMe <sub>3</sub>             | Br              | O |
| D.22 | H                     | CHMeCH <sub>2</sub> SiMe <sub>3</sub>             | CF <sub>3</sub> | O |
| D.23 | Propargyl             | CHMeCH <sub>2</sub> SiMe <sub>3</sub>             | Cl              | O |
| D.24 | Allenyl               | CHMeCH <sub>2</sub> SiMe <sub>3</sub>             | Cl              | O |
| D.25 | COMe                  | CHMeCH <sub>2</sub> SiMe <sub>3</sub>             | Cl              | O |
| D.26 | Propargyl             | CHMeCH <sub>2</sub> SiMe <sub>3</sub>             | Br              | O |
| D.27 | Allenyl               | CHMeCH <sub>2</sub> SiMe <sub>3</sub>             | Br              | O |
| D.28 | COMe                  | CHMeCH <sub>2</sub> SiMe <sub>3</sub>             | Br              | O |
| D.29 | COCH <sub>2</sub> OMe | CHMeCH <sub>2</sub> SiMe <sub>3</sub>             | Cl              | O |
| D.30 | COCH <sub>2</sub> OMe | CHMeCH <sub>2</sub> SiMe <sub>3</sub>             | CF <sub>3</sub> | O |
| D.31 | H                     | (CH <sub>2</sub> ) <sub>3</sub> SiMe <sub>3</sub> | Cl              | O |
| D.31 | H                     | (CH <sub>2</sub> ) <sub>3</sub> SiMe <sub>3</sub> | Br              | O |
| D.32 | H                     | (CH <sub>2</sub> ) <sub>3</sub> SiMe <sub>3</sub> | CF <sub>3</sub> | O |

Table 9 provides 32 compounds of formula (Ii) where R<sup>1</sup>, R<sup>6</sup>, R<sup>7</sup> and X are as defined in Table 9.



5 Table 10 provides 32 compounds of formula (Ij) where R<sup>1</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup> and X are as defined in Table 10.

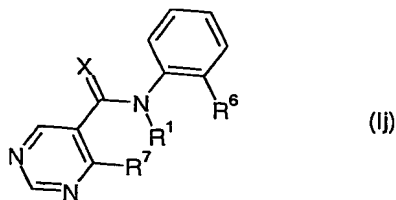
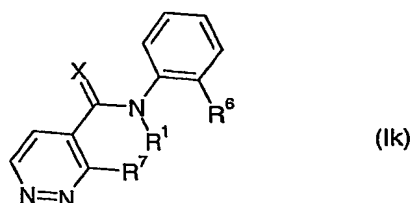


Table 11 provides 32 compounds of formula (Ik) where  $R^1$ ,  $R^6$ ,  $R^7$ ,  $R^8$ ,  $R^9$  and X are as defined in Table 11.



Throughout this description, temperatures are given in degrees Celsius; "NMR" means  
 5 nuclear magnetic resonance spectrum; MS stands for mass spectrum; and "%" is percent by weight, unless corresponding concentrations are indicated in other units.

The following abbreviations are used throughout this description:

|                          |                          |
|--------------------------|--------------------------|
| m.p. = melting point     | b.p.= boiling point.     |
| s = singlet              | br = broad               |
| d = doublet              | dd = doublet of doublets |
| t = triplet              | q = quartet              |
| m = multiplet            | ppm = parts per million  |
| qd = quartet of doublets | sext = sextet            |

Table 12 shows selected melting point and selected NMR data, all with  $CDCl_3$  as the  
 10 solvent (unless otherwise stated; if a mixture of solvents is present, this is indicated as, for example, ( $CDCl_3$  /  $d_6$ -DMSO)), (no attempt is made to list all characterising data in all cases) for compounds of Tables 1 to 11.

**Table 12**

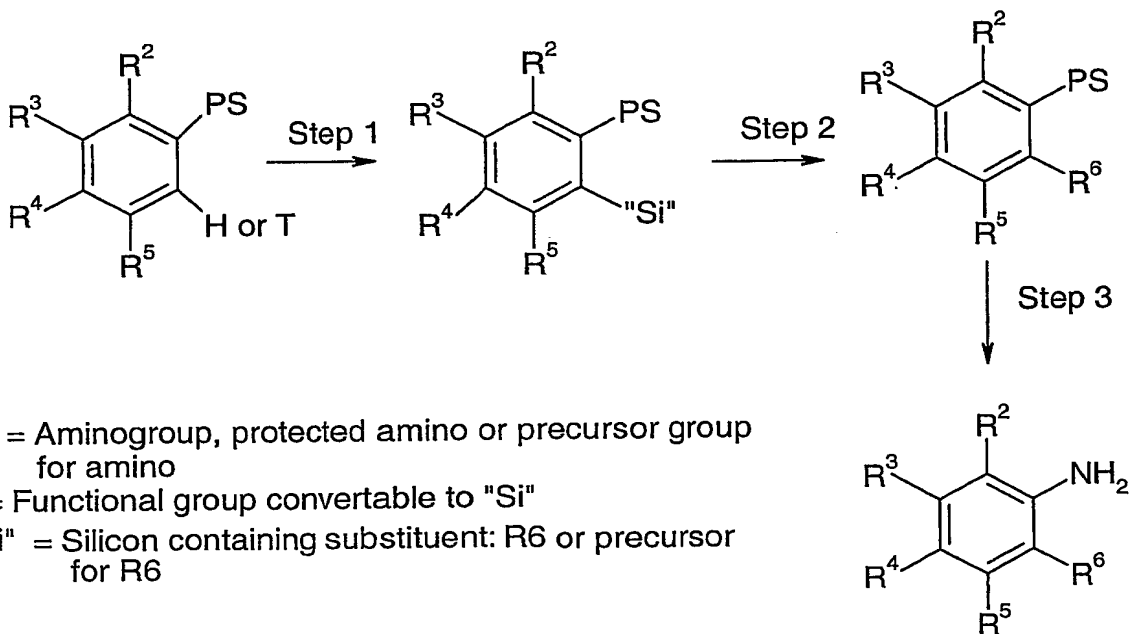
| Compound Number | $^1H$ -NMR data: (ppm/multiplicity/number of Hs).   | m.p. / ( $^{\circ}C$ ) |
|-----------------|---|------------------------|
| 1.1             | 0.0(s,9); 3.7(s,3); 7.0-7.5(m,5); 7.7(s,broad,1)  | 127-128                |
| 1.3             | 0.0(s,9); 2.3(s,2); 4.05(s,3); 7.15(m,3); 7.35(m,1); 8.5(s,1).  | 161-162                |
| 1.7             | -0.1(s,9); 1.3(d,3); 2.5(q,1 coinciding with DMSO signal); 4.0(s,3); 7.1-7.35(m,4); 8.5(s,1); 9.5(s,1). | 187-188                |

|      |  |             |
|------|--|-------------|
| 1.14 | 0.0(s,9); 0.8(m,2); 2.6(m,2); 4.05(s,3);<br>7.2-7.4(2m,3,1); 8.5(s,1); 9.7(s,1).   | 122-124     |
| 1.16 | 0.0(s,9); 0.8(m,2); 2.6(m,2); 3.9(s,3); 6.8(t,1)<br>7.1-7.3(m,3), 7.7-8.1(m,3).  | 109-111     |
| 1.20 | -0.1(s,9); 1.0(q of d,2); 1.2(d,3); 3.1(sext.1);<br>3.95(s,3); 7.2(m,2); 7.4(m,1); 7.6(br.s,1); 7.7(m,1);<br>8.1(s,1).           | 149-150     |
| 1.23 | -0.1(s,9); 1.0(q of d,2); 1.3(d,3); 3.2(sext.1);<br>3.95(s,3); 6.9(t,3); 7.2(m,2); 7.4(m,1); 7.7(m,1);<br>8.0(br.s,1); 8.1(s,1). | 124-126     |
| 1.43 | 0.1(s,9); 3.9(s,3); 5.5(s,1); 7.0(m,2); 7.2(m,2);<br>7.9(s,1); 7.95(br,1); 8.2(d,1).   | 100-101     |
| 2.3  | -0.1(s,9); 2.2(s,2); 3.7(s,3); 7.1-7.7(4m,2,1,1,1);<br>8.6(s,1).   | 124-126     |
| 2.7  | -0.1(s,9); 1.3(d,3); 2.5(q.1 coinciding with DMSO<br>signal); 3.7(s,3); 7.1-7.35(m,3); 7.45(d,1);<br>7.65(d,1); 9.3(s,1).        | 153-155     |
| 2.14 | 0.0(s,9); 0.8(m,2); 2.6(m,2); 3.75(s,3);<br>7.2-7.35(m,4); 7.45(s,1); 7.65(s,1); 9.4(s,1).                                       | 118-120     |
| 2.20 | -0.1(s,9); 1.0(q of d,2); 1.2(d,3); 3.1(sext,1);<br>3.7(s,3); 7.0(sd,1); 7.2(m,2); 7.35(m,2); 7.5(s,br,1);<br>7.8(m,1).          | 147-148     |
| 3.3  | 0.0(s,9); 2.15(s,2); 2.75(s,3); 7.1-7.25(m,3);<br>7.35(dd,1); 10.2(s,1).   | 125-128     |
| 3.7  | -0.1(s,9); 1.25(d,3); 2.5(q.1 coinciding with DMSO<br>signal); 2.7(s,3); 7.1-7.4(m,4); 10.3(s,1).                                | Viscous oil |
| 3.14 | 0.0(s,9); 0.8(m,2); 2.6(m,2); 2.8(s,3); 7.2-7.4(m,4);<br>10.3(s,1).  | 87-90       |
| 9.3  | 0.0(s,9); 2.25(s,2); 7.15(m,2); 7.5(dd,1); 7.6(dd,1);<br>8.0(dd,1); 8.6(dd,1); 10.0(s,1).  | 79-81       |

|      |   |         |
|------|---|---------|
| 9.14 | 0.0(s,9); 0.8(m,2); 2.65(m,2); 7.2-7.4(3m:2,1,1);<br>7.6(dd,1); 8.05(dd,1); 8.5(dd,1); 10.1(s,1).                   | 109-110 |
| 9.19 | 0.0(s,9); 1.0(q of d,2); 1.35(d,2); 3.25(sext,1);<br>7.2-7.5(2m,2,2); 7.8(m,1); 8.1(s,1). 8.35(dd,1);<br>8.6(dd,1). | 78.5-81 |

The compounds according to formula (I) may be prepared according to the following reaction schemes.

- 5 Some compounds of formula (II) are already known; novel compounds of formula (II) may be prepared according to the following synthetic strategies which are depicted in the following scheme and described below:



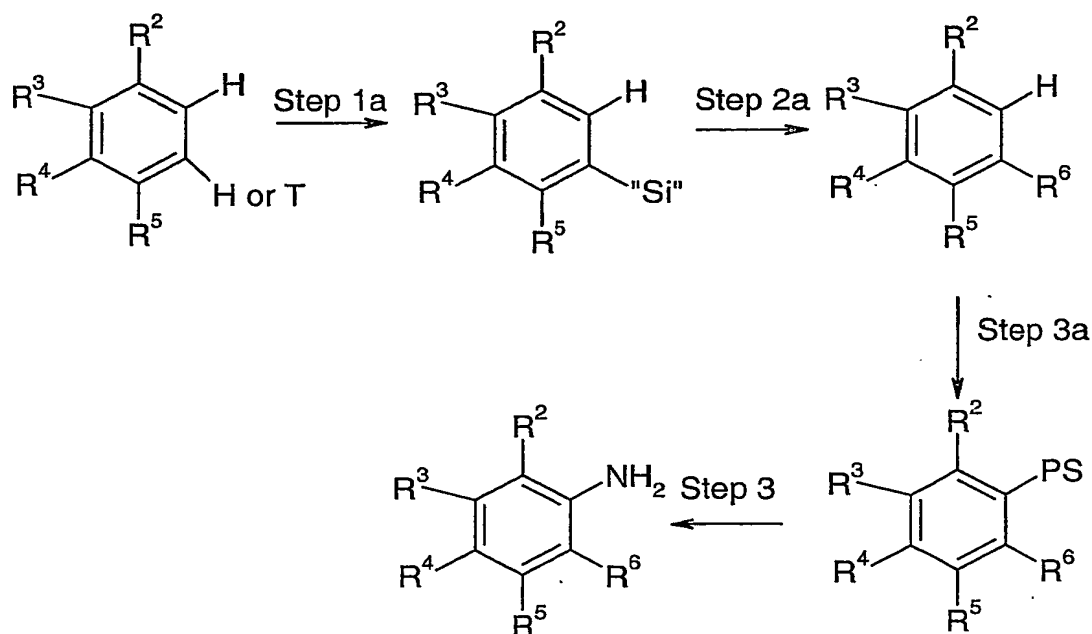
- 10 Step 1: Starting from a suitable precursor carrying a protected or free amino function or a substituent which may be converted to  $\text{NH}_2$  in a later stage of the synthesis (precursor substituent; PS) and, optionally, a substituent which is convertible to "Si", an appropriate Si-containing functionality ("Si") is introduced into the ortho position.

Step 2: If necessary, the introduced Si-containing group is further manipulated to form the desired substituent  $R^6$ .

Step 3: Deprotection if necessary or conversion of the precursor substituent to  $NH_2$ .

Steps 2 and 3 may also be carried out in reversed order.

- 5 It is also possible to perform step 1 and 2 on a phenyl derivative which is not substituted in a position ortho to the newly formed  $R^6$  (step 1a and 2a) and to introduce the  $NH_2$  or the precursor substituent PS afterwards (step 3a) [for example by nitration or via metalation followed by substitution].



10

Literature examples for the nitration of arylsilanes (for the situation where PS is nitro) can be found in E.A.Chernyshev et.al. *Izvestiya Akademii Nauk SSSR* **8**, 1424 (1960) and DE 1114641 (Union Carbide Corp.).

- 15 Examples of protecting groups for the  $NH_2$  functionality are formyl, acyl, haloacyl, trialkylsilyl, (substituted)benzyl and alkoxy carbonyl. A more comprehensive list of methods for protection and deprotection of anilines which are useful in the context of the present invention can be found in T.W. Green and P.G.M.Wuts, *Protective Groups in Organic Synthesis* 3<sup>rd</sup> edition p.503-614 (Wiley 1999).

Examples for precursor substituents PS are nitro and azido [both of which may be converted to  $\text{NH}_2$  by reduction or hydrogenation], carboxyl and carboxy derivatives [which may undergo rearrangements to form isocyanates, for example by Schmidt- or Hofmann-degradation] and halides and triflates [which may be converted to  $\text{NH}_2$  in protected or  
5 unprotected form via catalytic amination reactions currently known under the name "Buchwald Hartwig" reaction (for example X.Huang et al., *Org.Lett.* **3**, 3417 (2001) and references cited therein)].

More comprehensive lists for useful precursor substituents for  $\text{NH}_2$  can be found in Rodd's Chemistry of Carbon Compounds III B and its supplements (Elsevier 1974,1981 and  
10 1995) and in Compendium of Organic Synthetic Methods Vols.1-9 chapter 7 (Wiley 1971-2000).

For the introduction of Si-containing functionalities into phenyl derivatives (step 1) a large variety of synthetic methods are accessible. The chemist skilled in the art will understand that according to the methodology chosen for step 1 different groups T may be  
15 used. Examples of useful T substituents are halogens (such as Cl, Br and I), sulfonates (such as triflates, tosylates and mesylates), phosphates,  $\text{C}_{1-4}$  alkyl,  $\text{C}_{1-4}$  haloalkyl,  $\text{C}_{2-4}$  alkenyl,  $\text{C}_{2-4}$  haloalkenyl,  $\text{C}_{2-4}$  alkynyl,  $\text{C}_{1-4}$  alkylcarbonyl and  $\text{C}_{1-4}$  alkoxycarbonyl.

Manipulation of Si-containing functional groups (step 2) are widely known in the literature. Recent overviews can be found in The Chemistry of Organosilicon Compounds,  
20 Vols.1-3, S.Patay, Z.Rappaport and Z.Rappaport,Y.Apeloid eds. Wiley, 1989, 1998, 2001 and in Houben-Weyl Science of Synthesis, Organometallics Vol.4, I.Fleming ed., G.Thieme 2002. Examples of such manipulations which are especially relevant to the present invention are hydrogenation or reduction of double or triple bonds (or both) in the Si-containing group (please see later: Example 3, step B), cyclopropanation and epoxidation of said double bonds  
25 and functional group manipulation on the silicon atom (for example conversion of halogens to alkyl or alkoxy groups).

Literature examples which illustrate some of the methods which are especially relevant to the preparation of a compound of formula (II) include E.A.Chernyshev et. Al., *Bull.Acad. Sci.USSR* **1960**,1323; K.T. Kang et.al., *TL* **32**,4341 (1991) *Synth. Comm.* **24**,1507 (1994);  
30 M.Murata et al., *TL* **40**,9255 (1999); A.Falcou et.al., *Tetrahedron* **56**, 225 (2000); A. Arcadi et al., *TL* **27**, 6397 (1986); K.C.Nicolaou et al., *Chem.Eur.J.* **1**, 318 (1995); N.Chatani et al.,

JOC **60**, 834 (1995); T. Stuedemann et al., Tetrahedron **54**, 1299 (1998); P.F. Hurdlik et al., JOC **54**, 5613 (1989); K. Karabelas et al., JOC **51**, 5286 (1986); T. Jeffery, TL **40**, 1673 (1999) and TL **41**, 8445 (2000); K. Olofson et al., JOC **63**, 5076 (1998); H. Uirata et al., Bull. Chem. Soc. Jap. **57**, 607 (1984); and G. Maas et al., Tetrahedron **49**, 881 (1993); and  
5 references cited therein.

A compound of formula (I) may be prepared by reacting a compound of formula Het-C(=O)-R\* [where Het is as defined above for a compound of formula (I) and R\* is halogen, hydroxy or C<sub>1-6</sub> alkoxy, but preferably chloro] with a compound of formula (II), as defined above, in the presence of a base (such as triethylamine, Hunig base, sodium  
10 bicarbonate, sodium carbonate, potassium carbonate, pyridine or quinoline but preferably triethylamine or pyridine) and in a solvent (such as diethylether, TBME, THF, dichloromethane, chloroform, DMF or NMP) for between 10 minutes and 48 hours (preferably 12 to 24 hours) and between 0°C and reflux (preferably 20 to 25°C). When R\* is chloro, the reaction may also conveniently be carried out by a one-pot procedure by adding a reagent  
15 known to chlorinate carboxylic acids [such as thionyl chloride or oxalyl chloride] to a solution of Het-C(=O)-OH [where Het is as defined above for a compound of formula (I)] in an appropriate solvent (preferably diethylether, TBME, THF, dichloromethane, chloroform, tetrachloroethane or hexane) which contains a few drops of DMF as catalyst; removing any excess reagent by evaporation under reduced pressure; and adding the relevant compound of  
20 formula (II) and, optionally, more solvent as specified above to the crude heterocyclic acid chloride Het-C(=O)-R\* (where R\* is chloro). When R\* is hydroxy, a coupling agent [such as benzotriazol-1-yloxytris(dimethylamino) phosphoniumhexafluorophosphate, bis-(2-oxo-3-oxazolidinyl)-phosphinic acid chloride, N,N'-dicyclohexylcarbodiimide or 1,1'-carbonyl-diimidazole] may be used. When R\* is C<sub>1-6</sub> alkoxy, a stronger base [such as n-BuLi, LDA or,  
25 preferably, hexamethyldisilazanyl-Na (HMDS-Na)] may be used to activate the compound of formula (II).

A compound of formula (I) [where X is S] may be conveniently produced by treating a compound of formula (I) [where X is O] in an appropriate solvent (such as toluene or xylene) with a thionating agent (such as P<sub>2</sub>S<sub>5</sub> or Lawessons reagent) at elevated temperatures. An  
30 example of such a reaction can be found in WO 93/11117.

A compound of formula (I) [where R<sup>1</sup> is not hydrogen] may be prepared by:



either alkylation or acylation of a compound of formula (I) [where  $R^1$  is hydrogen] with a compound  $R^dL$  [where  $R^d$  is the desired substituent  $R^1$  and L is a common leaving group for alkylation or acylation reactions, for example halogen (such as Cl, Br, or I), a sulfonate (such as mesylate or tosylate), a quaternary ammonium group, formyloxy or an acyloxy group]. The reaction is preferably carried out in the presence of a strong base able to deprotonate the amide function of the compound of formula (I) or in the presence of an acylation catalyst (such as pyridine, a trialkylamine or dimethylaminopyridine) or in the presence of both a strong base and a catalyst. Alternatively a compound of formula (II) may be alkylated or acylated with  $R^dL$  [as defined above] and the resulting alkylated or acylated amine is treated with Het-C(=O)-R\* as described above.

Surprisingly, it has now been found that the novel compounds of formula (I) have, for practical purposes, a very advantageous spectrum of activities for protecting plants against diseases that are caused by fungi as well as by bacteria and viruses.

The compounds of formula (I) can be used in the agricultural sector and related fields of use as active ingredients for controlling plant pests. The novel compounds are distinguished by excellent activity at low rates of application, by being well tolerated by plants and by being environmentally safe. They have very useful curative, preventive and systemic properties and are used for protecting numerous cultivated plants. The compounds of formula (I) can be used to inhibit or destroy the pests that occur on plants or parts of plants (fruit, blossoms, leaves, stems, tubers, roots) of different crops of useful plants, while at the same time protecting also those parts of the plants that grow later e.g. from phytopathogenic microorganisms.

It is also possible to use compounds of formula (I) as dressing agents for the treatment of plant propagation material, in particular of seeds (fruit, tubers, grains) and plant cuttings (for example rice), for the protection against fungal infections as well as against phytopathogenic fungi occurring in the soil.

The compounds of formula (I) are, for example, effective against the phytopathogenic fungi of the following classes: Fungi imperfecti (e.g. Botrytis, Pyricularia, Helminthosporium, Fusarium, Septoria, Cercospora and Alternaria) and Basidiomycetes (for example Rhizoctonia, Hemileia, Puccinia). Additionally, they are also effective against the Ascomycetes classes (for example Venturia and Erysiphe, Podosphaera, Monilinia, Uncinula) and of the Oomycetes classes (for example Phytophthora, Pythium, Plasmopara). Outstanding activity has been

observed against powdery mildew (*Erysiphe* spp.). Furthermore, the novel compounds of formula I are effective against phytopathogenic bacteria and viruses (for example against *Xanthomonas* spp, *Pseudomonas* spp, *Erwinia amylovora* as well as against the tobacco mosaic virus).

5           Within the scope of present invention, target crops to be protected typically comprise the following species of plants: cereal (wheat, barley, rye, oat, rice, maize, sorghum and related species); beet (sugar beet and fodder beet); pomes, drupes and soft fruit (apples, pears, plums, peaches, almonds, cherries, strawberries, raspberries and blackberries); leguminous plants (beans, lentils, peas, soybeans); oil plants (rape, mustard, poppy, olives, sunflowers, coconut, 10 castor oil plants, cocoa beans, groundnuts); cucumber plants (pumpkins, cucumbers, melons); fibre plants (cotton, flax, hemp, jute); citrus fruit (oranges, lemons, grapefruit, mandarins); vegetables (spinach, lettuce, asparagus, cabbages, carrots, onions, tomatoes, potatoes, paprika); lauraceae (avocado, cinnamomum, camphor) or plants such as tobacco, nuts, coffee, eggplants, sugar cane, tea, pepper, vines, hops, bananas and natural rubber plants, as well as 15 ornamentals.

The compounds of formula (I) are used in unmodified form or, preferably, together with the adjuvants conventionally employed in the art of formulation. To this end they are conveniently formulated in known manner to emulsifiable concentrates, coatable pastes, directly sprayable or dilutable solutions, dilute emulsions, wettable powders, soluble powders, dusts, 20 granulates, and also encapsulations e.g. in polymeric substances. As with the type of the compositions, the methods of application, such as spraying, atomising, dusting, scattering, coating or pouring, are chosen in accordance with the intended objectives and the prevailing circumstances. The compositions may also contain further adjuvants such as stabilizers, antifoams, viscosity regulators, binders or tackifiers as well as fertilizers, micronutrient donors 25 or other formulations for obtaining special effects.

Suitable carriers and adjuvants can be solid or liquid and are substances useful in formulation technology, e.g. natural or regenerated mineral substances, solvents, dispersants, wetting agents, tackifiers, thickeners, binders or fertilizers. Such carriers are for example described in WO 97/33890.

30           The compounds of formula (I) are normally used in the form of compositions and can be applied to the crop area or plant to be treated, simultaneously or in succession with further

compounds. These further compounds can be e.g. fertilizers or micronutrient donors or other preparations which influence the growth of plants. They can also be selective herbicides as well as insecticides, fungicides, bactericides, nematocides, molluscicides or mixtures of several of these preparations, if desired together with further carriers, surfactants or application promoting adjuvants customarily employed in the art of formulation.

The compounds of formula (I) can be mixed with other fungicides, resulting in some cases in unexpected synergistic activities. Mixing components which are particularly preferred are azoles, such as azaconazole, BAY 14120, bitertanol, bromuconazole, cyproconazole, difenoconazole, diniconazole, epoxiconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, hexaconazole, imazalil, imibenconazole, ipconazole, metconazole, myclobutanil, pefurazoate, penconazole, pyrifenox, prochloraz, propiconazole, simeconazole, tebuconazole, tetraconazole, triadimefon, triadimenol, triflumizole, triticonazole; pyrimidinyl carbinole, such as ancymidol, fenarimol, nuarimol; 2-amino-pyrimidines, such as bupirimate, dimethirimol, ethirimol; morpholines, such as dodemorph, fenpropidine, fenpropimorph, spiroxamine, tridemorph; anilinopyrimidines, such as cyprodinil, mepanipyrim, pyrimethanil; pyrroles, such as fenpiclonil, fludioxonil; phenylamides, such as benalaxyl, furalaxyl, metalaxyl, R-metalaxyl, ofurace, oxadixyl; benzimidazoles, such as benomyl, carbendazim, debacarb, fuberidazole, thiabendazole; dicarboximides, such as chlozolate, dichlozoline, iprodione, myclozoline, procymidone, vinclozoline; carboxamides, such as carboxin, fenfuram, flutolanil, mepronil, oxycarboxin, thifluzamide; guanidines, such as guazatine, dodine, iminoctadine; strobilurines, such as azoxystrobin, kresoxim-methyl, metominostrobin, SSF-129, trifloxystrobin, picoxystrobin, BAS 500F (proposed name pyraclostrobin), BAS 520; dithiocarbamates, such as ferbam, mancozeb, maneb, metiram, propineb, thiram, zineb, ziram; N-halomethylthiotetrahydrophthalimides, such as captafol, captan, dichlofluanid, fluoromides, folpet, tolyfluanid; Cu-compounds, such as Bordeaux mixture, copper hydroxide, copper oxychloride, copper sulfate, cuprous oxide, mancopper, oxine-copper; nitrophenol-derivatives, such as dinocap, nitrothal-isopropyl; organo-p-derivatives, such as edifenphos, iprobenphos, isoprothiolane, phosdiphen, pyrazophos, tolclofos-methyl; various others, such as acibenzolar-S-methyl, anilazine, benthiavalicarb, blasticidin-S, chinomethionate, chloroneb, chlorothalonil, cyflufenamid, cymoxanil, dichlone, diclomezine, dicloran, diethofencarb, dimethomorph, SYP-LI90 (proposed name: flumorph), dithianon,

ethaboxam, etridiazole, famoxadone, fenamidone, fenoxanil, fentin, ferimzone, fluazinam, flusulfamide, fenhexamid, fosetyl-aluminium, hymexazol, iprovalicarb, IKF-916 (cyazofamid), kasugamycin, methasulfocarb, metrafenone, nicobifen, pencycuron, phthalide, polyoxins, probenazole, propamocarb, pyroquilon, quinoxifen, quintozone, sulfur, triazoxide, tricyclazole, triforine, validamycin, zoxamide (RH7281).

A preferred method of applying a compound of formula (I), or an agrochemical composition which contains at least one of said compounds, is foliar application. The frequency of application and the rate of application will depend on the risk of infestation by the corresponding pathogen. However, the compounds of formula I can also penetrate the plant through the roots via the soil (systemic action) by drenching the locus of the plant with a liquid formulation, or by applying the compounds in solid form to the soil, e.g. in granular form (soil application). In crops of water rice such granulates can be applied to the flooded rice field. The compounds of formula I may also be applied to seeds (coating) by impregnating the seeds or tubers either with a liquid formulation of the fungicide or coating them with a solid formulation.

A formulation [that is, a composition containing the compound of formula (I)] and, if desired, a solid or liquid adjuvant, is prepared in a known manner, typically by intimately mixing and/or grinding the compound with extenders, for example solvents, solid carriers and, optionally, surface active compounds (surfactants).

The agrochemical formulations will usually contain from 0.1 to 99% by weight, preferably from 0.1 to 95% by weight, of the compound of formula I, 99.9 to 1% by weight, preferably 99.8 to 5% by weight, of a solid or liquid adjuvant, and from 0 to 25% by weight, preferably from 0.1 to 25% by weight, of a surfactant.

Advantageous rates of application are normally from 5g to 2kg of active ingredient (a.i.) per hectare (ha), preferably from 10g to 1kg a.i./ha, most preferably from 20g to 600g a.i./ha. When used as seed drenching agent, convenient dosages are from 10mg to 1g of active substance per kg of seeds.

Whereas it is preferred to formulate commercial products as concentrates, the end user will normally use dilute formulations.

The following non-limiting Examples illustrate the above-described invention in more detail.

EXAMPLE 1

This Example illustrates the preparation of Compound Number 1.14.

0.5g 2-(2'-Trimethylsilylethyl)aniline (A.Falcou et.al., Tetrahedron 56, 225 (2000)) and 0.55g 1-methyl-3-trifluoromethyl-4-chlorocarbonyl-pyrazole were combined in THF under cooling with ice and then 0.21ml pyridine were added. After warming to ambient temperature, the mixture was stirred for 3.5 hours, poured into water and extracted twice with ethylacetate. Separation of the organic phase, drying over sodiumsulfate and evaporation of the solvent yielded 0.9g (94.7%) of Compound Number 1.14.

EXAMPLE 2

This Example illustrates the preparation of Compound Number 2.14.

To 0.5g 1-methyl-4-trifluoromethyl-pyrrole-3-carboxylic acid dissolved in 10ml dichloromethane containing 2 drops of dimethylformamide 0.24ml thionylchloride was slowly added at room temperature. The solution, which soon turned dark, was stirred for 3hours at room temperature and was then slowly added to a solution of 0.5g 2-(2'-trimethylsilyl-ethyl)aniline and 0.54ml triethylamine in 10ml dichloromethane at room temperature. After stirring for 18hours, the solvent was removed under reduced pressure and the residue taken up in ethylacetate. Washing with water and brine, drying over sodiumsulfate and evaporation of the solvent yielded 1.08 g of a dark oil, which was purified by FC (flash-chromatography) over silica gel (eluent: hexane/ethylacetate 2:1). The yield was 0.3g of Compound Number 2.14 (31.6%).

EXAMPLE 3

This Example illustrates the preparation of Compound Number 1.20.

Step A: Preparation of 2-(2-Nitrophenyl)-3-(trimethylsilyl)-2-propene.

2-Iodonitrobenzene [19.7g] and triethylamine [15.6ml] were dissolved in dimethylformamide [33ml]. 1-Trimethylsilylpropin-1 [4.9ml] and bis(triphenylphosphin)-palladiumdichloride [1.16g] were then added at room temperature in a nitrogen atmosphere. After stirring for 5minutes, formic acid [3.25ml] was added dropwise. Once the initial exothermic reaction had terminated the mixture was held at 60°C over night. After cooling, the yellow reaction mixture was poured into a mixture of ethylacetate [350ml] and water [350ml], stirred for 1hour and then the organic phase was collected and washed with water. The product was distilled off under reduced pressure and the residue was purified by

chromatography on silicagel (eluent: 5% ethylacetate in hexane) to yield 7.2g of a yellow oil which was used in the next step without further purification.

Step B: Preparation of 2-(2-Aminophenyl)-3-(trimethylsilyl)-propane.

The reaction product of step A [7.2g] was hydrogenated in tetrahydrofuran over palladium on charcoal at atmospheric pressure and room temperature until the uptake of hydrogen ceased. The catalyst was filtered off and, after evaporation of the solvent, the product was chromatographed on silicagel (eluent: 10% ethylacetate in hexane) to yield 2-(2-aminophenyl)-3-(trimethylsilyl)-propane [4.7g; 88% purity according to NMR]. This product was used in the next step without further purification.

Step C:

To a solution of 2-(2-aminophenyl)-3-(trimethylsilyl)-propane [11g] and 1-methyl-3-(trifluoromethyl)-pyrazol-4-carbonylchloride [10.15g] in tetrahydrofuran [150ml], pyridine [3.85ml] was added whilst cooling with ice. The mixture was stirred at ambient temperature over night to give a yellow suspension. The solvent was evaporated under reduced pressure and then water and ethylacetate were added and the organic phase was collected, washed with saturated brine and dried. Evaporation of the solvent yielded Compound Number 1.20 which was recrystallised from a mixture of hexane and toluene. Yield: 13.55g; mp.149-150°C.

EXAMPLE 4

This Example illustrates the preparation of Compound Number 2.20.

2-(2-Aminophenyl)-3-(trimethylsilyl)-propane (25g; purity 85%), 1-methyl-3-(trifluoromethyl)-pyrrole-4-carboxylic acid [19.8g] and triethylamine [28.6g] were dissolved in dichloromethane [500ml] and then bis(2-oxo-3-oxazolidinyl)phosphinicacid chloride [26.1g] was added with ice cooling. The reaction mixture was allowed to warm to room temperature and stirred overnight. Most of the solvent was evaporated under reduced pressure and then the residue was diluted with ethylacetate [1000ml] and twice washed with saturated sodiumbicarbonate solution and brine. After drying with sodium sulfate the solvent was evaporated to yield crude Compound Number 2.20; recrystallisation from hexane and toluene yielded 14.1g of the desired product, m.p.147-148°C.

FORMULATION EXAMPLES FOR COMPOUNDS OF FORMULA (I)

Working procedures for preparing formulations of the compounds of formula I such as Emulsifiable concentrates, Solutions, Granulates, Dusts and Wettable powders are described in WO 97/33890.

Biological Examples: Fungicidal actionsExample B-1: Action against *Puccinia recondita* / wheat (Brownrust on wheat)

1 week old wheat plants cv. Arina are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. One day after application wheat plants are inoculated by spraying a spore suspension ( $1 \times 10^5$  uredospores/ml) on the test plants. After an incubation period of 2 days at 20°C and 95% r. h. plants are kept in a greenhouse for 8 days at 20°C and 60% r.h. The disease incidence is assessed 10 days after inoculation.

Infestation is prevented virtually completely (0-5% infestation) with each of Compounds 1.14, 2.14, 3.14, and 9.14.

Example B-2: Action against *Podosphaera leucotricha* / apple (Powdery mildew on apple)

5 week old apple seedlings cv. McIntosh are treated with the formulated test compound (0.002% active ingredient) in a spray chamber. One day after application apple plants are inoculated by shaking plants infected with apple powdery mildew above the test plants. After an incubation period of 12 days at 22°C and 60% r.h. under a light regime of 14/10 hours (light/dark) the disease incidence is assessed.

Compounds 1.3, 1.14, 2.3, 2.14, 3.3, 3.14, 9.3 and 9.14 each exhibit strong efficacy (<20% infestation).

Example B-3: Action against *Venturia inaequalis* / apple (Scab on apple)

4 week old apple seedlings cv. McIntosh are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. One day after application apple plants are inoculated by spraying a spore suspension ( $4 \times 10^5$  conidia/ml) on the test plants. After an incubation period of 4 days at 21°C and 95% r.h. the plants are placed for 4 days at 21°C and 60% r.h. in a greenhouse. After another 4 day incubation period at 21°C and 95% r.h. the disease incidence is assessed.

Compounds 1.14, 2.14, 3.14, and 9.14 each exhibit strong efficacy (<20% infestation).

Example B-4: Action against *Erysiphe graminis* / barley (Powdery mildew on barley)

1 week old barley plants cv. Express were treated with the formulated test compound (0.02% active ingredient) in a spray chamber. One day after application barley plants were inoculated by shaking powdery mildew infected plants above the test plants. After an incubation period of 6 days at 20°C / 18°C (day/night) and 60%r.h. in a greenhouse the disease incidence was assessed.

Compounds 1.14, 2.14, 3.14, and 9.14 each exhibit strong efficacy (<20% infestation).

Example B-5: Action against *Botrytis cinerea* / grape (Botrytis on grapes)

5 week old grape seedlings cv. Gutedel were treated with the formulated test compound (0.002% active ingredient) in a spray chamber. Two days after application grape plants were inoculated by spraying a spore suspension ( $1 \times 10^6$  conidia/ml) on the test plants. After an incubation period of 4 days at 21°C and 95%r.h. in a greenhouse the disease incidence was assessed.

Compounds 1.3, 1.14, 2.3, 2.14, 3.3, 3.14, 9.3 and 9.14 show good activity in this test (<50% disease incidence).

Example B-6: Action against *Botrytis cinerea* / tomato (Botrytis on tomatoes)

4 week old tomato plants cv. Roter Gnom were treated with the formulated test compound (0.002% active ingredient) in a spray chamber. Two days after application tomato plants were inoculated by spraying a spore suspension ( $1 \times 10^5$  conidia/ml) on the test plants. After an incubation period of 4 days at 20°C and 95%r.h. in a growth chamber the disease incidence was assessed.

Compounds 1.3, 1.14, 2.3, 2.14, 3.3, 3.14, 9.3 and 9.14 each exhibit strong efficacy (<20% disease incidence).

Example B-8: Action against *Septoria nodorum* / wheat (Septoria leaf spot on wheat)

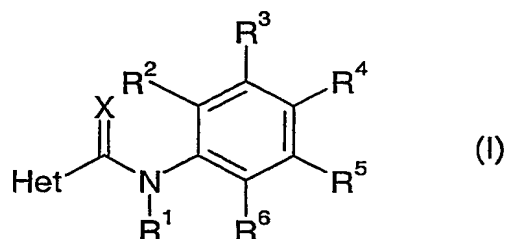
1 week old wheat plants cv. Arina were treated with the formulated test compound (0.02% active ingredient) in a spray chamber. One day after application wheat plants were inoculated by spraying a spore suspension ( $5 \times 10^5$  conidia/ml) on the test plants. After an incubation period of 1 day at 20°C and 95%r.h. plants are kept for 10 days at 20°C and 60%r.h. in a greenhouse. The disease incidence was assessed 11 days after inoculation.

Compounds 1.3, 1.14, 2.3, 2.14, 3.3, 3.14, 9.3 and 9.14 show good activity in this test (<50% disease incidence).



CLAIMS

1. A compound of formula (I):



where

Het is a 5- or 6-membered heterocyclic ring containing one to three heteroatoms, each independently selected from oxygen, nitrogen and sulphur, the ring being substituted by groups  $R^7$ ,  $R^8$  and  $R^9$ ;

$R^1$  is hydrogen, optionally substituted  $(C_{1-4})$ alkyl, optionally substituted  $(C_{1-4})$ alkylC(=O), optionally substituted  $(C_{1-4})$ alkylC(=O)O, optionally substituted  $(C_{1-4})$ alkoxy $(C_{1-4})$ alkyl, optionally substituted allyl, optionally substituted propargyl or optionally substituted allenyl;

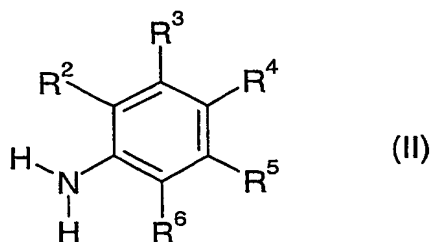
$R^2$ ,  $R^3$ ,  $R^4$  and  $R^5$  are each, independently, hydrogen, halogen, optionally substituted  $(C_{1-4})$ alkyl, optionally substituted  $(C_{1-4})$ alkoxy or optionally substituted  $(C_{1-4})$ alkoxy $(C_{1-4})$ alkyl;

$R^6$  is an aliphatic or alicyclic, saturated or unsaturated group containing three to thirteen carbon atoms and at least one silicon atom and, optionally, one to three heteroatoms, each independently selected from oxygen, nitrogen and sulphur, and is optionally substituted by one to four independently selected halogen atoms;

$R^7$ ,  $R^8$  and  $R^9$  are each, independently, hydrogen, halogen,  $C_{1-3}$  alkyl,  $C_{1-3}$  haloalkyl,  $C_{1-3}$ alkoxy $(C_{1-3})$ alkyl or cyano, where at least one of  $R^7$ ,  $R^8$  and  $R^9$  is not hydrogen; and X is O or S;

or an N-oxide thereof.

2. A compound of formula (II):



where

5  $R^2, R^3, R^4$  and  $R^5$  are each, independently, hydrogen, halogen,  $\text{CH}_3$ ,  $\text{CF}_3$  or  $\text{OCF}_3$ ;

$R^6$  is  $(\text{CHR}^{10})(\text{CR}^{11}\text{R}^{12})_r\text{Si}(\text{R}^{13})(\text{R}^{14})(\text{R}^{15})$ ;

$r$  is 0, 1, 2 or 3;

$R^{10}$  is  $\text{C}_{1-3}$  alkyl or  $\text{C}_{1-3}$  haloalkyl; but if  $r$  is 2 or 3 then  $R^{10}$  may be also hydrogen;

each  $R^{11}$  and each  $R^{12}$  is, independently, chosen from hydrogen, halogen,  $\text{C}_{1-3}$  alkyl and

10  $\text{C}_{1-3}$  haloalkyl;

$R^{13}, R^{14}$  are, independently, methyl or ethyl; and  $R^{15}$  is  $\text{C}_{1-6}$  alkyl,  $\text{C}_{1-4}$  alkoxy( $\text{C}_{1-4}$ )alkyl,

$\text{C}_{1-3}$  haloalkyl,  $\text{C}_{2-6}$  alkenyl or  $\text{C}_{1-6}$  alkoxy;

or  $R^{10}$  and  $R^{11}$  on adjacent carbon atoms or two  $R^{11}$  groups on adjacent carbon atoms may together be a double bond or with the carbon atoms to which they are attached may

15 form cyclopropyl which is optionally substituted by up to two substituents,

independently chosen from halogen and methyl; or any two  $R^{11}$  groups or  $R^{10}$  and any

one  $R^{11}$  may, together with the carbon atoms through which they are linked, form a

cycloalkyl ring of ring size 4-7 which optionally contains 1 heteroatom selected from

oxygen and sulfur and which is optionally substituted by up to two substituents,

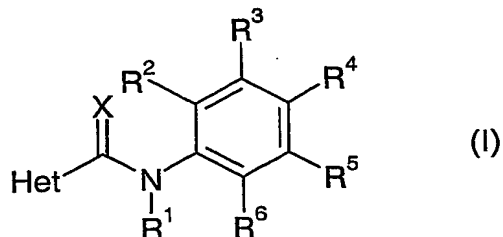
20 independently chosen from halogen and methyl; provided that  $R^6$  is such that the total

number of C atoms is 5-13, the total number of halogen atoms is 0-4 and the number of heteroatoms is 0-3.

- 3 A composition for controlling microorganisms and preventing attack and infestation of plants therewith, wherein the active ingredient is a compound of formula (I) as claimed in claim 1 together with a suitable carrier.
- 5 4 A method of controlling or preventing infestation of cultivated plants by phytopathogenic microorganisms by application of a compound of formula (I) as claimed in claim 1 to plants, to parts thereof or the locus thereof.

ABSTRACT  
CHEMICAL COMPOUNDS

A compound of formula (I):



5

where Het is a 5- or 6-membered heterocyclic ring containing one to three heteroatoms, each independently selected from oxygen, nitrogen and sulphur, the ring being substituted by groups  $R^7$ ,  $R^8$  and  $R^9$ ;  $R^1$  is hydrogen, optionally substituted (C<sub>1-4</sub>)alkyl, optionally substituted (C<sub>1-4</sub>)alkylC(=O), optionally substituted (C<sub>1-4</sub>)alkylC(=O)O, optionally substituted (C<sub>1-4</sub>)alkoxy(C<sub>1-4</sub>)alkyl, optionally substituted allyl, optionally substituted propargyl or optionally substituted allenyl;  $R^2$ ,  $R^3$ ,  $R^4$  and  $R^5$  are each, independently, hydrogen, halogen, optionally substituted (C<sub>1-4</sub>)alkyl, optionally substituted (C<sub>1-4</sub>)alkoxy or optionally substituted (C<sub>1-4</sub>)alkoxy(C<sub>1-4</sub>)alkyl;  $R^6$  is an aliphatic or alicyclic, saturated or unsaturated group containing three to thirteen carbon atoms and at least one silicon atom and, optionally, one to three heteroatoms, each independently selected from oxygen, nitrogen and sulphur, and is optionally substituted by one to four independently selected halogen atoms;  $R^7$ ,  $R^8$  and  $R^9$  are each, independently, hydrogen, halogen, C<sub>1-3</sub> alkyl, C<sub>1-3</sub> haloalkyl, C<sub>1-3</sub>alkoxy(C<sub>1-3</sub>)alkyl or cyano, where at least one of  $R^7$ ,  $R^8$  and  $R^9$  is not hydrogen; and X is O or S; or an N-oxide thereof. The compounds of formula (I) have plant-protective properties and are suitable for protecting plants against infestations by phytopathogenic microorganisms.

20

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